The Open University

SM358

Chapter Summaries

This document collects together summaries from the chapters of all three books of SM358. It may provide a useful compact source of reference when you revise for the exam. Please note that you are not expected to memorize all the equations in these summaries because the exam paper will be accompanied by an *Equations List*. It is advisable to be familiar with the layout of the *Equations List*, and to recognize the meaning and uses of the equations that it contains.

Book 1 Chapter 1

Section 1 Microscopic systems on the scale of molecules, atoms, nuclei and subnuclear particles have discrete energy levels. Transitions between these energy levels involving the emission or absorption of photons are a prime source of information concerning the structure of matter. Systems such as ionized atoms have a continuum of energy levels above the highest discrete level of the bound system.

Section 2 The world is not deterministic; observations involving photons, electrons, etc. are probabilistic. Radioactive decay provides an example: identical nuclei of a specific kind have a well-defined probability of decaying, but the instant of decay of an individual nucleus is unpredictable. A practical application of quantum indeterminism is the quantum random number generator based on the random appearance of photons on either side of a half-silvered mirror. A characteristic feature of the quantum world, which reappears in every chapter in different forms, is this: quantum physics predicts a fixed overall pattern of some kind, but individual events occur randomly within that pattern.

Section 3 Light exhibits 'wave–particle duality' i.e. it exhibits both wave-like and particle-like behaviour. Photons are not simply packets of electromagnetic radiation, but have momentum and energy, and are detected in localized regions.

Section 4 Electrons and indeed all material particles also exhibit wave–particle duality, displaying either wave or particle aspects depending on the type of experiment to which they are subjected. The de Broglie wavelength is related to momentum by $\lambda = h/p$. The propagation of a particle as a wave is described by a complex-valued wave function which obeys an equation called Schrödinger's equation. In one dimension, the wave function is usually represented by $\Psi(x, t)$. Its significance is understood as follows: the probability of detecting a particle at time t in a small interval δx, centred on position x, is $|\Psi(x, t)|^2 \, \delta x$.

Section 5 To allow for the interference of two terms in a wave function, it is essential to add the two terms *before* taking the square of the modulus. More generally, squaring the modulus of a probability amplitude gives a probability. The interference rule states that when a given process can happen in two or more alternative (but unrecorded) ways, the probability amplitudes for the different ways must be added before taking the square of the modulus.

Section 6 Quantum physics has fundamentally changed our understanding of the world. Do not be surprised if quantum mechanics seems shocking; its creators found it so!

Book 1 Chapter 2

Section 1   A key task is to establish the equation that governs the time-development of the wave function. This is Schrödinger's equation. It is possible to guess the form of Schrödinger's equation for a de Broglie wave describing a free particle of energy $\hbar\omega$ and momentum $\hbar k$.

Section 2   To extend Schrödinger's equation to particles subject to forces, several mathematical concepts are needed, including operators (specifically linear operators) and eigenvalue equations, which take the form $\widehat{A}f(x) = \lambda f(x)$.

Section 3   In wave mechanics each observable is associated with a linear operator, and the only possible outcomes of a measurement of an observable are the eigenvalues of the corresponding operator. For example, the momentum component p_x is represented by the linear operator $\widehat{p}_x = -i\hbar\partial/\partial x$. A de Broglie wave is an eigenfunction of both the kinetic energy and the momentum operators.

Schrödinger's equation for a system can be written down using a three-step recipe. Step 1: write down the Hamiltonian function of the system. This is the energy of the system, including kinetic and potential energies, but with the kinetic energy written in terms of momentum. Step 2: replace all classical observables by the corresponding operators to obtain the Hamiltonian operator. Step 3: write down Schrödinger's equation in the compact form:

$$i\hbar\frac{\partial\Psi}{\partial t} = \widehat{H}\Psi,$$

and expand the right-hand side by applying the appropriate Hamiltonian operator to a wave function that depends on the coordinates of all the particles, and on time.

Section 4   The wave function $\Psi(x,t)$, a solution of Schrödinger's equation, is complex and cannot be measured. It provides the most complete specification possible of the state of a system. The probability of finding the particle in that state in a small interval δx, centred on x, is $|\Psi(x,t)|^2\,\delta x$ (Born's rule), provided that the wave function has been normalized. Wave functions which differ by an overall multiplicative phase factor describe the same state. Since Schrödinger's equation involves only linear operators, a linear combination of two solutions is also a solution. This is the superposition principle.

Section 5   Schrödinger's equation for a particle moving in one-dimension with potential energy $V(x)$ is satisfied by product wave functions of the form $\Psi(x,t) = \psi(x)T(t)$. The method of separation of variables shows that $T(t)$ has the universal form $e^{-iEt/\hbar}$, while $\psi(x)$ satisfies the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x).$$

If the energy of the system is measured in a state described by the product wave function $\psi(x)\,e^{-iEt/\hbar}$, the value E will be observed with certainty.

The time-independent Schrödinger equation is an eigenvalue equation for energy:

$$\widehat{H}\psi(x) = E\psi(x).$$

Insisting that the energy eigenfunctions $\psi(x)$ should not diverge as x approaches $\pm\infty$ ensures that, if $V(x)$ is a finite well, the energy eigenvalues between the bottom and the top of the well are discrete while those above the top of the well form a continuum. The product wave functions are usually called stationary-state wave functions because they lead to probability distributions that are independent of time. Those corresponding to the continuum are not physically acceptable since they cannot be normalized. However, some linear combinations of stationary-state wave functions, known as wave packets, can be normalized and can be used to describe the non-stationary states associated with the continuum.

Book 1 Chapter 3

Section 3.1   A particle of mass m in a one-dimensional infinite square well, with walls at $x = 0$ and $x = L$, has an infinite set of discrete energy levels

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad \text{for } n = 1, 2, 3, \ldots,$$

with corresponding normalized energy eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } 0 \le x \le L,$$

$$\psi_n(x) = 0 \quad \text{outside the well.}$$

The stationary-state wave functions

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-iE_n t/\hbar} \quad \text{for } 0 \le x \le L,$$

are complex standing waves describing states of definite energy, E_n.

These solutions are obtained by separating variables in the Schrödinger equation and solving the time-independent Schrödinger equation, subject to continuity boundary conditions. These conditions require that the energy eigenfunction $\psi(x)$ is continuous everywhere, and that $d\psi/dx$ is continuous at points where the potential energy function is finite. At the walls of an infinite square well we only require the continuity of $\psi(x)$, and this leads to energy quantization.

Shifting the walls of the well without altering its width, or assigning a different constant potential energy to the bottom of the well, will change the way the system is described, but not the way it behaves. Each energy eigenfunction in a one-dimensional *symmetric* well is either even or odd.

Section 3.2 The infinite square well can be generalized to two and three dimensions. For a three-dimensional infinite square well that occupies a cubic region of width L, the energy eigenvalues are given by

$$E_{n_x,n_y,n_z} = \frac{(n_x^2 + n_y^2 + n_z^2)\pi^2\hbar^2}{2mL^2}.$$

If the well occupies the region $0 \le x \le L$, $0 \le y \le L$ and $0 \le z \le L$, the corresponding normalized energy eigenfunctions are

$$\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x\pi x}{L}\right) \sin\left(\frac{n_y\pi y}{L}\right) \sin\left(\frac{n_z\pi z}{L}\right).$$

A three-dimensional infinite square well can be used to model the energy levels in F-centres and quantum dots. In two and three dimensions, energy levels may be degenerate.

Section 3.3 The time-independent Schrödinger equation for a particle in a finite one-dimensional square well can be solved numerically. For negative energies (below the top of the well) a finite number of energy eigenvalues and eigenfunctions are obtained. Energy quantization arises from the continuity boundary conditions, which now require both $\psi(x)$ and $d\psi/dx$ to be continuous at the walls of the well. The eigenfunctions, and the corresponding stationary-state wave functions, extend beyond the walls of the well. This means that there is a non-zero probability of finding the particle outside the well — a characteristic quantum phenomenon called *barrier penetration*. This phenomenon is observed in the case of a deuteron, whose constituent particles have a root-mean-square separation that is about twice the range of the force that binds them together.

Book 1 Chapter 4

Section 4.1 In wave mechanics, the state of a system is completely specified by its wave function. The time-evolution of the wave function is fully predicted by Schrödinger's equation. Nevertheless, quantum mechanics is indeterministic because the result of measuring an observable in a state described by a given wave function is unpredictable. The act of measurement drastically alters the state of the system, so the wave function after the measurement is not the same as the wave function before the measurement. To test the predictions of quantum physics, we often take a large number of *identical* systems all in the *same* state, and perform the *same* measurement on each system.

Not everything in quantum mechanics is unpredictable. Every energy measurement yields one or other of the energy eigenvalues. In a stationary state corresponding to the energy eigenvalue E_i, we are certain to obtain the energy E_i.

Section 4.2   We consider a system with a discrete set of non-degenerate energy eigenvalues (a particle in a one-dimensional infinite well). If the energy of a system is measured at time t, then the probability of obtaining the ith energy eigenvalue E_i is given by the overlap rule

$$p_i = \left| \int_{-\infty}^{\infty} \psi_i^*(x)\, \Psi(x,t)\, \mathrm{d}x \right|^2,$$

where $\Psi(x,t)$ is the wave function of the system at the instant of measurement, and $\psi_i(x)$ is the energy eigenfunction with eigenvalue E_i. Both the wave function and the eigenfunction are assumed to be normalized. For this rule to be consistent, energy eigenfunctions with different eigenvalues must be orthogonal to one another.

If, at the time of measurement, the wave function is a linear combination of energy eigenfunctions, then the probability of obtaining the energy eigenvalue E_i is given by $|c_i(t)|^2$, where $c_i(t)$ is the coefficient of the energy eigenfunction $\psi_i(x)$ in the wave function.

These rules can be extended to other observables and systems.

Section 4.3   If an observable A has a discrete set of possible values, the expectation value of A in a given state Ψ is defined by

$$\langle A \rangle = \sum_i p_i a_i,$$

where p_i is the probability of obtaining value a_i in the state Ψ. Expectation values can be calculated using the sandwich integral rule

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\, \widehat{\mathrm{A}}\, \Psi(x,t)\, \mathrm{d}x.$$

Sections 4.4 and 4.5   The uncertainty of an observable A is defined by

$$\Delta A = \left\langle (A - \langle A \rangle)^2 \right\rangle^{1/2} = \left(\langle A^2 \rangle - \langle A \rangle^2 \right)^{1/2}.$$

With this definition, the Heisenberg uncertainty principle states that

$$\Delta x \, \Delta p_x \geq \frac{\hbar}{2}.$$

Book I Chapter 5

Section 5.1   Classical simple harmonic motion involves sinusoidal oscillations in response to a restoring force that is proportional to the displacement of a particle from an equilibrium position. The angular frequency of the oscillation is $\omega_0 = \sqrt{C/m}$, where C is the force constant and m is the mass of the particle.

The internal motion of a two-particle system, composed of particles of masses m_1 and m_2, can be analyzed by considering the motion of a single particle with the *reduced* mass $\mu = m_1 m_2 / (m_1 + m_2)$.

Section 5.2   The time-independent Schrödinger equation for a harmonic oscillator takes the form

$$-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2 \psi_n}{\mathrm{d}x^2} + \tfrac{1}{2} m \omega_0^2 x^2 \psi_n = E_n \psi_n.$$

The energy eigenvalues form an evenly-spaced ladder

$$E_n = (n + \tfrac{1}{2})\hbar\omega_0 \quad \text{for } n = 0, 1, 2, \ldots,$$

but transitions that involve the absorption or emission of photons are effectively restricted to those between neighbouring energy levels.

The corresponding energy eigenfunctions take the form

$$\psi_n(x) = C_n H_n(x/a)\, \mathrm{e}^{-x^2/2a^2},$$

where C_n is a normalization constant, $H_n(x/a)$ is an nth order Hermite polynomial in x/a, and $\mathrm{e}^{-x^2/2a^2}$ is a Gaussian function. The constant $a = \sqrt{\hbar/m\omega_0}$ is the length parameter that characterizes the oscillator.

The energy eigenfunction $\psi_n(x)$ has n nodes; it is even when n is even, and odd when n is odd. The energy eigenfunctions form an orthonormal set.

Section 5.3   The Hamiltonian operator for a harmonic oscillator can be expressed as

$$\widehat{H} = \left(\widehat{A}^\dagger \widehat{A} + \tfrac{1}{2} \right) \hbar \omega_0,$$

where $\widehat{A}^\dagger$ and $\widehat{A}$ are raising and lowering operators. These operators convert any energy eigenfunction into a neighbouring eigenfunction. If the eigenfunctions are normalized, then

$$\widehat{A}\,\psi_n(x) = \sqrt{n}\,\psi_{n-1}(x) \quad \text{and} \quad \widehat{A}^\dagger \psi_{n-1}(x) = \sqrt{n}\,\psi_n(x).$$

By using this representation, and repeatedly applying $\widehat{A}^\dagger$ to the ground state, it is possible to generate all the eigenfunctions and eigenvalues.

Section 5.4   Expectation values and uncertainties of x and p_x are conveniently calculated by expressing $\widehat{x}$ and $\widehat{p}_x$ in terms of the raising and lowering operators, and using the commutation relation $\widehat{A}\,\widehat{A}^\dagger - \widehat{A}^\dagger\,\widehat{A} = 1$. The selection rule for radiative transitions in vibrating molecules can also be derived using raising and lowering operators.

Book I Chapter 6

Section 6.1   A wave packet is a normalized linear combination of two or more stationary-state wave functions. Because of the superposition principle, wave packets satisfy Schrödinger's equation. Unlike stationary states, wave packets have probability densities that change in time, and so can describe motion.

In a harmonic oscillator, the probability density associated with a wave packet can oscillate to-and-fro with the classical frequency. Other types of motion, such as symmetrical breathing in and out are also possible. The expectation values of position and momentum are either permanently equal to zero, or oscillate sinusoidally with time.

Section 6.2   Ehrenfest's theorem states that

$$\frac{\mathrm{d}\langle x \rangle}{\mathrm{d}t} = \frac{\langle p_x \rangle}{m} \quad \text{and} \quad \frac{\mathrm{d}\langle p_x \rangle}{\mathrm{d}t} = - \left\langle \frac{\partial V}{\partial x} \right\rangle.$$

This theorem is always true. The classical limit corresponds to a wave packet with narrow spreads of position and momentum, subject to a force that varies slowly over the width of the wave packet. In this limit, the predictions of quantum mechanics approach those of classical mechanics.

Section 6.3   Given an initial wave function $\Psi(x,0)$, it is possible to predict the time-development of this wave function using a three-step procedure. We illustrated this for a harmonic oscillator. First, we expanded the initial state as a sum of energy eigenfunctions $\psi_i(x)$ of the oscillator. This is always possible because these eigenfunctions form a complete set. Then we determined the coefficients in the expansion, using the overlap integral

$$a_i = \int_{-\infty}^{\infty} \psi_i^*(x)\Psi(x,0)\,\mathrm{d}x.$$

Finally, we introduced time-dependent phase factors into the sum, replacing each energy eigenstate $\psi_i(x)$ by the corresponding stationary-state wave function $\psi_i(x)\,\mathrm{e}^{-\mathrm{i}E_i t/\hbar}$. This provides a solution of Schrödinger's equation that obeys the initial conditions, and so is the wave function we were looking for.

Section 6.4   Free-particle wave packets can be constructed by taking a continuous linear combination of de Broglie wave functions:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k)\mathrm{e}^{\mathrm{i}(kx - E_k t/\hbar)}\,\mathrm{d}k.$$

This wave packet is normalized provided that the function $A(k)$ obeys the condition $\int_{-\infty}^{\infty} |A(k)|^2\,\mathrm{d}k = 1$. The coefficients $A(k)$ are called momentum amplitudes. They are interpreted with the aid of Born's rule for momentum, which states that the probability of obtaining a momentum in a small interval of momentum $\hbar\,\delta k$, centred on $\hbar k$, is $|A(k)|^2\,\delta k$.

The time development of a free-particle wave packet can be predicted using an extension of the three-step procedure used for a harmonic oscillator. For a free particle, the overlap integral becomes a Fourier transform:

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0)\mathrm{e}^{-\mathrm{i}kx}\,\mathrm{d}x.$$

By analyzing the motion of a free-particle wave packet, we predicted how a Gaussian packet spreads with time, and (in a computer simulation) how a single-slit diffraction pattern is formed.

Book 1 Chapter 7

Introduction   Scattering is a process in which incident particles interact with a target and are changed in nature, number, speed or direction of motion as a result. Tunnelling is a quantum phenomenon in which particles that are incident on a classically impenetrable barrier are able to pass through the barrier and emerge on the far side of it.

Section 7.1   In one dimension, wave packets scattered by finite square barriers or wells generally split into transmitted and reflected parts, indicating that there are non-zero probabilities of both reflection and transmission. These probabilities are represented by the reflection and transmission coefficients R and T. The values of R and T generally depend on the nature of the target and the properties of the incident particles. If there is no absorption, creation or destruction of particles, $R + T = 1$.

Section 7.2   Unnormalizable stationary-state solutions of Schrödinger's equation can be interpreted in terms of steady beams of particles. A term such as $A\mathrm{e}^{\mathrm{i}(kx-\omega t)}$ can be associated with a beam of linear number density $n = |A|^2$ travelling with speed $v = \hbar k/m$ in the direction of increasing x. Such a beam has intensity $j = nv$. In this approach, $T = j_{\text{trans}}/j_{\text{inc}}$ and $R = j_{\text{ref}}/j_{\text{inc}}$.

For particles of energy $E_0 > V_0$, incident on a finite square step of height V_0, the transmission coefficient is

$$T = \frac{4k_1 k_2}{(k_1 + k_2)^2},$$

where

$$k_1 = \frac{\sqrt{2mE_0}}{\hbar} \quad \text{and} \quad k_2 = \frac{\sqrt{2m(E_0 - V_0)}}{\hbar}$$

are the wave numbers of the incident and transmitted beams. For a finite square well or barrier of width L, the transmission coefficient can be expressed as

$$T = \frac{4E_0(E_0 \pm V_0)}{4E_0(E_0 \pm V_0) + V_0^2 \sin^2(k_2 L)},$$

where $k_2 = \sqrt{2m(E_0 \pm V_0)}/\hbar$, with the plus signs being used for a well and the minus signs for a barrier. Transmission resonances, at which $T = 1$ and the transmission is certain, occur when $k_2 L = N\pi$ where N is an integer.

Travelling wave packets and steady beams of particles can both be thought of as representing flows of probability. In one dimension such a flow is described by the probability current

$$j_x(x,t) = -\frac{\mathrm{i}\hbar}{2m}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x}\right).$$

In three dimensions, scattering is described by the total cross-section, σ, which is the rate at which scattered particles emerge from the target per unit time per unit incident flux. For any chosen direction, the differential cross-section tells us the rate of scattering into a small cone of angles around that direction. At very high energies, total cross-sections are dominated by inelastic effects due to the creation of new particles.

Section 7.3   Wave packets with a narrow range of energies centred on E_0 can tunnel though a finite square barrier of height $V_0 > E_0$. In a stationary-state approach, solutions of the time-independent Schrödinger equation in the classically forbidden region contain exponentially growing and decaying terms of the form $C\mathrm{e}^{-\alpha x}$ and $D\mathrm{e}^{\alpha x}$, where $\alpha = \sqrt{2m(V_0 - E_0)}/\hbar$ is the attenuation coefficient. The transmission coefficient for tunnelling through a finite square barrier of width L and height V_0 is approximately

$$T \simeq 16\left(\frac{E_0}{V_0}\right)\left(1 - \frac{E_0}{V_0}\right)\mathrm{e}^{-2\alpha L} \qquad \text{provided that } \alpha L \gg 1.$$

Such a transmission probability is small and decreases rapidly as the barrier width L increases.

Section 7.4   Square barriers and wells are poor representations of the potential energy functions found in Nature. However, if the potential $V(x)$ varies smoothly as a function of x, the transmission coefficient for tunnelling of energy E_0 can be roughly represented by

$$T \approx \exp\left(-2\int_{r_0}^{r_1} \frac{\sqrt{2m(V(r) - E_0)}}{\hbar}\,\mathrm{d}x\right).$$

This approximation can be used to provide a successful theory of nuclear alpha decay as a tunnelling phenomenon. It can also account for the occurrence of nuclear fusion in stellar cores, despite the relatively low temperatures there. In addition, it explains the operation of the scanning tunnelling microscope which can map surfaces on the atomic scale.

Book 2 Chapter 1

Section 1.1   The state of a quantum system can be represented by a ket vector in an abstract vector space called function space. For wave mechanics in one dimension, the inner product is given by

$$\langle f|g\rangle = \int_{-\infty}^{\infty} f^*(x)\, g(x)\, \mathrm{d}x.$$

This inner product is a complex number with the properties

$$\langle f|g\rangle^* = \langle g|f\rangle, \quad \langle f|cg\rangle = c\,\langle f|g\rangle \quad \text{and} \quad \langle cf|g\rangle = c^*\,\langle f|g\rangle,$$

and it obeys the inequalities

$$\langle f|f\rangle \geq 0 \quad \text{and} \quad \langle f|f\rangle\langle g|g\rangle \geq |\langle f|g\rangle|^2.$$

Section 1.2   The Dirac bracket $\langle f|g\rangle$ can be regarded as a joining together of a bra vector $\langle f|$ and a ket vector $|g\rangle$. It is important to remember that the ket vector $|g\rangle = \sum_i c_i\,|g_i\rangle$ corresponds to the bra vector $\langle g| = \sum_i c_i^*\,\langle g_i|$, and vice versa.

Section 1.3   Observable quantities are represented by linear Hermitian operators. By definition, an operator $\widehat{A}$ is Hermitian if

$$\langle \widehat{A}f|g\rangle = \langle f|\widehat{A}g\rangle$$

for all normalizable functions f and g. Hermitian operators have real expectation values and real eigenvalues. If two eigenfunctions (or eigenvectors) of a Hermitian operator correspond to different eigenvalues, they are orthogonal.

If $\widehat{A}$ and $\widehat{B}$ are Hermitian, the product $\widehat{A}\widehat{B}$ is Hermitian if and only if $\widehat{A}$ commutes with $\widehat{B}$. Any power of $\widehat{A}$ is Hermitian, $\widehat{A}\widehat{B} + \widehat{B}\widehat{A}$ is Hermitian, and any linear combination $\alpha\widehat{A} + \beta\widehat{B}$ is Hermitian *provided that* the constants α and β are real.

Section 1.4   The generalized Ehrenfest theorem states that the rate of change of the expectation value of an observable is

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \frac{1}{i\hbar}\left\langle \left[\widehat{A}, \widehat{H}\right]\right\rangle, \qquad \left(\text{Note: } [\widehat{A},\widehat{H}] = \widehat{A}\widehat{H} - \widehat{H}\widehat{A}\right)$$

where $\widehat{H}$ is the Hamiltonian operator of the system, and the expectation values on both sides of the equation are calculated for the same state. If $\widehat{A}$ commutes with $\widehat{H}$, the expectation value of A remains constant in time, no matter what state the system is in. This leads to the quantum-mechanical versions of the laws of conservation of energy and momentum. Such conservation laws can be related to symmetries of the system.

Section 1.5   The generalized uncertainty principle states that

$$\Delta A\, \Delta B \geq \tfrac{1}{2}\left|\left\langle [\widehat{A}, \widehat{B}]\right\rangle\right|,$$

where ΔA and ΔB are the uncertainties of any two observables A and B in a given state, and the right-hand side involves the expectation value of the commutator of $\widehat{A}$ and $\widehat{B}$ in the given state.

Book 2 Chapter 2

Section 2.1   In classical physics, the z-component of the angular momentum of a particle is $L_z = xp_y - yp_z$. The x- and y-components can be obtained from this by a cyclic permutation of the subscripts: $x \Longrightarrow y \Longrightarrow z \Longrightarrow x$. The magnitude of the angular momentum of a rigid body rotating about a fixed axis is $L = I\omega$, where I is the

moment of inertia about the axis and ω is the angular speed of the body. The corresponding rotational energy is $E_{\text{rot}} = L^2/2I$.

Section 2.2   Many atoms, nuclei and particles behave as magnetic dipoles, characterized by a magnetic dipole moment $\boldsymbol{\mu}$. In a magnetic field $\mathbf{B}$, a magnetic dipole has potential energy $E_{\text{mag}} = -\boldsymbol{\mu} \cdot \mathbf{B}$. In a non-uniform magnetic field pointing in the z-direction, a magnetic dipole experiences a force $F_z = \mu_z\, \partial B_z/\partial z$. The magnetic dipole moment due to an orbiting charge is related to the orbital angular momentum by $\boldsymbol{\mu} = \gamma\mathbf{L}$, where γ is the gyromagnetic ratio.

The Stern–Gerlach experiment shows that the magnetic dipole moments of atoms are quantized. Because of the intimate link between magnetic dipole moments and angular momentum, the experiment also provides evidence for the quantization of angular momentum.

Section 2.3   The quantum-mechanical operator for the z-component of angular momentum is $\widehat{L}_z = (-i\hbar)(x\,\partial/\partial y - y\,\partial/\partial x)$. Similar results for $\widehat{L}_x$ and $\widehat{L}_y$ are obtained by cyclic permutation of the subscripts. In spherical coordinates,

$$\widehat{L}_z = -i\hbar \frac{\partial}{\partial \phi}.$$

The eigenfunctions of $\widehat{L}_z$ are of the form $A\,e^{im\phi}$, and single-valuedness imposes the requirement that m is an integer (positive, negative or zero). The corresponding eigenvalues are $m\hbar$.

The square of the magnitude of angular momentum is represented by the operator $\widehat{L}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2$. This has eigenvalues $l(l+1)\hbar^2$, where l is any non-negative integer. Using these eigenvalues we can explain the infrared absorption spectrum of HCl, caused by transitions between rotational energy levels.

Section 2.4   The expectation value L_z remains constant in time if $\widehat{L}_z$ commutes with the Hamiltonian operator of the system. The expectation values of all the components of angular momentum are conserved if the Hamiltonian operator is spherically symmetric. This is an example of the profound link between symmetries and conservation laws.

Section 2.5   Mutually commuting Hermitian operators have simultaneous eigenfunctions. Angular momentum operators obey the commutation relations

$$\left[\widehat{L}_x, \widehat{L}_y\right] = i\hbar\,\widehat{L}_z \quad \text{and} \quad \left[\widehat{L}_z, \widehat{L}^2\right] = 0,$$

with similar results obtained by cyclic permutation. Apart from an exceptional case, where all three angular momentum components are equal to zero, it is impossible for any two components of angular momentum to have definite values in the same state. However, it is possible to find states $|l, m\rangle$ that are simultaneous eigenfunctions of $\widehat{L}_z$ and $\widehat{L}^2$, with

$$\widehat{L}_z|l, m\rangle = m\hbar|l, m\rangle \quad \text{and} \quad \widehat{L}^2|l, m\rangle = l(l+1)\hbar^2|l, m\rangle.$$

For a given value of l, the values of m are restricted to $m = 0, \pm 1, \pm 2, \dots, \pm l$.

The energy eigenfunctions of any spherically-symmetric system can be chosen to be simultaneous eigenfunctions of $\widehat{H}, \widehat{L}_z$ and $\widehat{L}^2$.

Section 2.6   The two lines appearing in the Stern–Gerlach experiment for silver atoms cannot be explained by the otherwise successful theory. They point to a distinct (non-orbital) kind of angular momentum called spin.

Book 2 Chapter 3

Section 3.1   Any spin component of a spin-$\frac{1}{2}$ particle has two possible values, $+\hbar/2$ and $-\hbar/2$, corresponding to the two beams that emerge from a Stern–Gerlach magnet. The probability that an atom will be measured to be spin-up relative to one Stern–Gerlach magnet, when it has been prepared to be spin-up relative to another Stern–Gerlach magnet, is equal to $\cos^2(\theta/2)$, where θ is the angle between the orientation vectors of the two magnets.

Section 3.2   The spin state of a spin-$\frac{1}{2}$ particle is represented by a vector in spin space, which can be conveniently written as a two-element matrix called a spinor. The inner product of $|A\rangle = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}$ and $|B\rangle = \begin{bmatrix} b_1 \\ b_2 \end{bmatrix}$ is given by

$$\langle A|B\rangle = \begin{bmatrix} a_1^* & a_2^* \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \end{bmatrix} = a_1^* b_1 + a_2^* b_2.$$

As always, we have $\langle A|B\rangle^* = \langle B|A\rangle$.

Section 3.3 The spin component in a given direction **n** is an observable quantity, represented in quantum mechanics by a 2×2 matrix

$$\widehat{S}_{\mathbf{n}} = \frac{\hbar}{2} \begin{bmatrix} \cos\theta & e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & -\cos\theta \end{bmatrix}.$$

This matrix has eigenvectors

$$|\uparrow_{\mathbf{n}}\rangle = \begin{bmatrix} \cos(\theta/2) \\ e^{i\phi}\sin(\theta/2) \end{bmatrix} \quad \text{and} \quad |\downarrow_{\mathbf{n}}\rangle = \begin{bmatrix} -e^{-i\phi}\sin(\theta/2) \\ \cos(\theta/2) \end{bmatrix},$$

and eigenvalues $+\hbar/2$ and $-\hbar/2$. The two eigenvectors form an orthonormal basis in spin space. They are the only states that have definite values of the spin component in the **n**-direction.

Spin matrices along different Cartesian axes obey commutation relations similar to those for the components of orbital angular momentum. As a result, it is impossible for two (different and non-opposite) components of spin to have definite values in the same state. The matrix $\widehat{S}^2 = \widehat{S}_x^2 + \widehat{S}_y^2 + \widehat{S}_z^2$ commutes with all spin matrices and has the value $s(s+1)\hbar^2$ in any state, where $s = 1/2$. This is the origin of the term 'spin-$\frac{1}{2}$ particle'.

Section 3.4 Spin components are undetermined until they are measured. On measurement of $S_{\mathbf{n}}$, the spin state vector collapses onto an eigenvector of $\widehat{S}_{\mathbf{n}}$ — the one whose eigenvalue is equal to the value obtained in the measurement.

If a particle is in the spin state

$$|A\rangle = a_{\mathrm{u}}|\uparrow_{\mathbf{n}}\rangle + a_{\mathrm{d}}|\downarrow_{\mathbf{n}}\rangle,$$

and the spin component in the **n**-direction is measured, the probability of getting the spin-up value $+\hbar/2$ is $|a_{\mathrm{u}}|^2 = |\langle\uparrow_{\mathbf{n}}|A\rangle|^2$, and the probability of getting the spin-down value $-\hbar/2$ is $|a_{\mathrm{d}}|^2 = |\langle\downarrow_{\mathbf{n}}|A\rangle|^2$. Detailed calculations confirm the $\cos^2(\theta/2)$ rule.

The expectation value of $S_{\mathbf{n}}$ is given by the sandwich rule $\langle S_{\mathbf{n}}\rangle = \langle A|\widehat{S}_{\mathbf{n}}|A\rangle$.

Section 3.5 A spin-$\frac{1}{2}$ particle in a magnetic field $\mathbf{B} = B\mathbf{n}$ has the Hamiltonian matrix $\widehat{H} = -\gamma_{\mathrm{s}} B \widehat{S}_{\mathbf{n}}$, where γ_{s} is the spin gyromagnetic ratio of the particle.

The time-independent Schrödinger equation has two energy eigenvectors that are the eigenvectors of $\widehat{S}_{\mathbf{n}}$: $|\uparrow_{\mathbf{n}}\rangle$ and $|\downarrow_{\mathbf{n}}\rangle$, and two energy eigenvalues, $\pm\hbar\omega/2$, where $\omega = |\gamma_{\mathrm{s}}|B$ is the Larmor frequency. The (time-dependent) Schrödinger equation is solved by expanding the initial spin state in terms of $|\uparrow_{\mathbf{n}}\rangle$ and $|\downarrow_{\mathbf{n}}\rangle$. The time-dependent spin-state is then obtained by inserting appropriate factors of $e^{\pm i\omega t/2}$.

Book 2 Chapter 4

Section 4.1 The Hamiltonian operator $\widehat{H} = \widehat{H}_1 + \widehat{H}_2$ for a system of two non-interacting particles is a sum of Hamiltonian operators associated with the individual particles. It acts on a wave function $\Psi(x_1, x_2, t)$ that depends on the coordinates of both particles.

For two distinguishable particles, Born's rule states that the probability of finding particle 1 in a small interval δx_1, centred on x_1, *and* particle 2 in a small interval δx_2, centred on x_2, is $|\Psi(x_1, x_2, t)|^2 \, \delta x_1 \, \delta x_2$.

Separating the space and time variables in Schrödinger's equation, we obtain stationary state solutions which are the product of an energy eigenfunction $\psi(x_1, x_2)$ and a time-dependent phase factor, $e^{-iEt/\hbar}$. Solving the time-independent Schrödinger equation for a system of two non-interacting *distinguishable* particles gives energy eigenfunctions of the form $\psi(x_1, x_2) = \psi_n(x_1)\psi_k(x_2)$, where n and k are quantum numbers of single-particle states with eigenvalues E_n and E_k, and $E_n + E_k = E$. For distinguishable spin-$\frac{1}{2}$ particles, a more complete description is provided by the total wave function $\psi_{1,2} = \psi(x_1, x_2)|m_{s_1}, m_{s_2}\rangle$. Operators that depend on coordinates and momenta act on the spatial part of the total wave function, while spin operators act on the spin part.

Section 4.2 In the quantum world, all particles sharing the same set of unalterable attributes are *identical*. All electrons are identical, for example. Any particle can be classified as being either a boson or a fermion. For identical bosons, the total wave function is always *symmetric* (unchanged by swapping a pair of particle labels);

for identical fermions, the total wave function is always *antisymmetric* (reversed in sign by swapping the particle labels).

The spatial part of the total wave function must either be symmetric ($\psi^+(x_1, x_2)$) or antisymmetric ($\psi^-(x_1, x_2)$), where

$$\psi^\pm(x_1, x_2) = \frac{1}{\sqrt{2}}\big[\psi_n(x_1)\,\psi_k(x_2) \pm \psi_k(x_1)\,\psi_n(x_2)\big].$$

Both these possibilities are consistent with the fact that the probability density is independent of the scheme used to label the particles.

The spin part of the total wave function must also be symmetric or antisymmetric. For identical spin-$\frac{1}{2}$ particles, the possibilities are:

symmetric: $\quad \dfrac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad |\uparrow\uparrow\rangle, \quad |\downarrow\downarrow\rangle,$

antisymmetric: $\quad \dfrac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).$

These spin states are eigenfunctions of the total spin operators $\widehat{S}^2$ and $\widehat{S}_z$, and they can be classified in terms of the eigenvalues $S(S+1)\hbar^2$ and $M_S\hbar$ of these operators. Writing them in the same order as before, we have:

symmetric: $\quad |1, 0\rangle, \quad |1, 1\rangle, \quad |1, -1\rangle,$

antisymmetric: $\quad |0, 0\rangle.$

The three symmetric states are called *triplet states* and have $S = 1$, and the antisymmetric state is called the *singlet state* and has $S = 0$.

Bosons are particles of integer spin ($s = 0, 1, 2, \ldots$). Fermions are particles of half-integer spin ($s = 1/2, 3/2, 5/2, \ldots$). For example, photons are bosons, and electrons, protons and neutrons are fermions. Composite particles made up of an odd number of fermions are fermions; those made up of an even number of fermions are bosons. Composite particles made up exclusively of bosons are bosons.

Systems of bosons are represented by symmetric total wave functions, so the spin and spatial parts have the same symmetry (both symmetric or both antisymmetric). Systems of identical fermions are represented by antisymmetric total wave functions, so the spin and spatial parts have opposite symmetries. A pair of electrons in a symmetric (i.e. triplet) spin state is represented by an antisymmetric spatial wave function $\psi^-(x_1, x_2)$. A pair of electrons in the antisymmetric (i.e. singlet) spin state is represented by a symmetric spatial wave function $\psi^+(x_1, x_2)$.

The probability densities for systems of identical particles differ markedly from those for non-identical particles. Both the overall spin state and the boson/fermion nature of the particles matter. Identical bosons in a symmetric spin state show a marked tendency to 'crowd together', as do identical fermions in an antisymmetric spin state. However, identical bosons in an antisymmetric spin state and identical fermions in a symmetric spin state show the contrary tendency: they avoid each other. These effects arise from the symmetry or antisymmetry of the wave function and are not connected with forces acting between the particles.

Section 4.3 As a result of the antisymmetry of their total wave function, identical fermions obey the Pauli exclusion principle: no two identical fermions can be in the same quantum state, with the same set of quantum numbers (including those associated with spin). The Pauli exclusion principle has profound effects on the chemical and physical properties of matter. For example, it explains the incompressibility of metals and the stability of white dwarf stars.

A Bose–Einstein condensate is a phase of matter formed by boson-type atoms at extremely low temperatures, when their de Broglie wavelengths become comparable to the inter-atomic spacing. At a critical temperature, a phase transition takes place in which many of the atoms 'condense' into the lowest energy single-particle state. These atoms form the Bose–Einstein condensate, which behaves in many respects like a single entity, described by a macroscopic wave function, $\Psi(\mathbf{r}, t)$.

Book 2 Chapter 5

The principles of quantum mechanics

States

1a The state of a system is specified by a normalized state vector $|\Psi\rangle$.

1b The vector $e^{i\alpha}|\Psi\rangle$, where α is a real number, represents the same physical state as $|\Psi\rangle$.

1c If $|\Psi_1\rangle$ and $|\Psi_2\rangle$ represent possible states of a system, and c_1 and c_2 are complex constants, the normalized linear combination $c_1|\Psi_1\rangle + c_2|\Psi_2\rangle$
also represents a possible state of the system.

States of identical particles

2a All particles in Nature fall into two categories: fermions and bosons. For fermions, the spin quantum number s is equal to an odd multiple of $1/2$; for bosons, s is equal to an integer (including zero).

2b Composite particles with an odd number of fermions are fermions; composite particles with an even number of fermions are bosons.

2c The total wave function of a collection of identical fermions is antisymmetric under exchange of particle labels; this leads to the Pauli exclusion principle. The total wave function of a collection of identical bosons is symmetric under exchange of particle labels; this leads to Bose–Einstein condensation at low temperatures.

Observables

3 Observables are represented by linear Hermitian operators.

Measurements and their results

The next three principles apply to observables with discrete sets of values:

4a The possible measured values of an observable A are the eigenvalues of the corresponding quantum-mechanical operator, $\widehat{A}$.

5a For a system in a state represented by the normalized state vector $|\Psi\rangle$, the probability that a measurement of A will yield the result a_i is $p_i = \left|\langle a_i|\Psi\rangle\right|^2$, where $|a_i\rangle$ is the normalized eigenvector corresponding to the eigenvalue a_i. This is the overlap rule.

6a The state of the system immediately after a measurement is represented by the normalized eigenvector $|a_i\rangle$ that corresponds to the eigenvalue a_i that was obtained in the measurement. This collapse of the state vector, leading from the state on which the measurement is made to $|a_i\rangle$, cannot be described by Schrödinger's equation and is accompanied by an irreversible change in the measuring device.

These principles can be extended to observables with continuous ranges of values:

4b The possible measured values of any observable A are the set of numbers that are generalized eigenvalues of the corresponding quantum-mechanical operator, $\widehat{A}$.

5b The overlap rule can be generalized to an observable with a continuous set of values, leading to Born's rules for position and momentum.

6b A fine-resolution measurement of an observable with a continuum of possible values causes the state vector to collapse onto a narrow wave packet centred on the value obtained in the measurement, with a width determined by the resolution of the measurement.

Time-development in the absence of measurement

7 Provided that a system does not interact with a measuring device, its time-development is governed by Schrödinger's equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\Psi\rangle = \widehat{H}|\Psi\rangle,$$

where $|\Psi\rangle$ represents the state of the system at time t, and $\widehat{H}$ is the Hamiltonian operator of the system.

Book 2 Chapter 6

Section 6.1   Do quantum systems have properties before they are measured? This fundamental question, raised in this section, is an ongoing question for the rest of the chapter.

Section 6.2   A two-particle system is in an entangled state if its state vector cannot be expressed as a product of terms representing each particle, and so neither particle on its own has definite properties, though the pair does. Entangled states exhibit non-locality — Einstein's 'spooky action at a distance' — a deeply non-classical property. An example is provided by the singlet state of a pair of spin-$\frac{1}{2}$ particles. A significant property of singlet states is that they have a similar form in all bases; as a result, for whatever angle the spin component of one particle is measured, the spin component of the second particle, measured at the same angle, will be the opposite. Entanglement is not restricted to the spin states of pairs of particles; it also applies to spatial states and to photons.

Section 6.3   Entanglement can be studied experimentally. Bohm's hypothetical experiment involves the singlet state of a pair of spin-$\frac{1}{2}$ particles. According to quantum mechanics, such a pair of singlet states exhibits correlations that *cannot* be exhibited by any system governed by local hidden variables (Bell's theorem). In this sense, Nature is non-local. The question is whether Nature obeys the laws of quantum mechanics or satisfies some limits – Bell's inequalities – satisfied by any system with local hidden variables.

Section 6.4   Experiments to test for hidden variables have been carried out involving polarized light (photons). The quantum description of such polarization is rather like the quantum description of spin-$\frac{1}{2}$ particles, with some differences (mainly $\theta/2 \rightarrow \theta$). Two experiments are described: the classic experiments of Aspect and colleagues carried out in the early 1980s, and the more recent experiments involving entangled states of three photons. In each case, the quantum-mechanical predictions are decisively reproduced: Nature is non-local and there are no local hidden variables.

Section 6.5   Entanglement is of great current interest and may be regarded as a fundamental resource of nature. Practical applications will be discussed in the next chapter.

Book 2 Chapter 7

Section 7.1   The polarization of photons is a major vehicle for the transport of quantum information. Polarizing beam analyzers can be used to measure the linear polarization of a photon relative to a given polarizer axis, with the possible outcomes being vertical polarization (value $+1$) and horizontal polarization (value -1). The corresponding quantum-mechanical operator $\widehat{\mathcal{P}}(\theta)$ has eigenvectors $|V_\theta\rangle$ and $|H_\theta\rangle$, with eigenvalues $+1$ and -1. These eigenvectors form a basis for any state of linear polarization of a photon.

Section 7.2   Quantum key distribution, QKD, enables the secure transmission of information. The essential idea is that quantum measurements, unlike classical measurements, inevitably disturb the measured system. Quantum protocols for quantum cryptography have been devised to exploit this fact. Any eavesdropper would inevitably collapse the state of quantum particles bearing the transmitted information. The BB84 protocol does not involve entanglement, but another protocol, based on a proposal due to Artur Eckert, uses entanglement in an essential way. Both methods have been shown to work and are being developed for commercial applications.

Section 7.3   Quantum teleportation is the exact transfer of the unknown quantum state of a particle (usually a photon) to a distant particle. At first sight, three features of quantum mechanics appear to make this difficult. Firstly, it is impossible to measure an arbitrary state of a system exactly, without disturbing it. Secondly, the no-cloning theorem tells us that the linearity of operators in quantum mechanics forbids the cloning of states. Thirdly, quantum bits (or qubits) contain an infinite amount of information. Nevertheless, another feature of quantum mechanics — entanglement — can be exploited to make teleportation work.

One scheme for teleporting the state of a single photon (labelled 1) involves creating a separate entangled pair of photons (labelled 2 and 3) and using a beam splitter to combine photons 1 and 2. By making a Bell state measurement, the distant photon 3 can be collapsed onto a state that is closely related to the original state of photon 1. Classical communication can inform the recipient of photon 3 what needs to be done to it to make its state the same as the initial state of photon 1. The first successful teleportation experiment succeeded in teleporting the state of 25% of the photons. This limitation was due to the fact that only one of the four 'Bell state measurements' is straightforward.

Section 7.4   A quantum computer stores information in entangled linear superpositions of quantum states. Although sensitive to external disturbances, quantum computers may allow massively parallel processing,

allowing special classes of problem (including the factoring of large numbers) to be solved in cases that are beyond the powers of ordinary computers.

Book 3 Chapter 1

Section 1.1   This section gave a brief review of facts about orbital angular momentum from Chapter 2 of Book 2.

Section 1.2   Ignoring spin, the time-independent Schrödinger equation for a particle in a spherically-symmetric potential energy well is separable in spherical coordinates. It has product solutions $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$, which are also eigenfunctions of $\widehat{L}^2$ and $\widehat{L}_z$:

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R_{nl}}{\mathrm{d}r}\right) + \frac{l(l+1)\hbar^2}{2mr^2}R_{nl}(r) + V(r)R_{nl}(r) = E_{nl}R_{nl}(r)$$

$$\widehat{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 \, Y_{lm}(\theta, \phi)$$

$$\widehat{L}_z Y_{lm}(\theta, \phi) = m\hbar \, Y_{lm}(\theta, \phi),$$

where the orbital angular momentum quantum number $l = 0, 1, 2, \ldots$, and the magnetic quantum number $m = -l, -l+1, \ldots, l-1, l$. The ability to label the energy eigenfunctions in this way is consistent with the fact that the Hamiltonian operator $\widehat{H}$, $\widehat{L}^2$ and $\widehat{L}_z$ form a mutually-commuting set. The term $l(l+1)\hbar^2/2mr^2$ is called the centrifugal barrier; it tends to keep particles with high angular momentum away from the origin.

Section 1.3   The functions $Y_{lm}(\theta, \phi)$ are spherical harmonics. They can be written as $Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\mathrm{e}^{\mathrm{i}m\phi}$. The restrictions on the quantum numbers m and l arise from the need to ensure that $Y_{lm}(\theta, \phi)$ is single-valued and finite. Spherical harmonics are orthonormal

$$\int_0^{2\pi}\int_0^{\pi} Y_{l_1 m_1}^*(\theta, \phi)\, Y_{l_2 m_2}(\theta, \phi)\, \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \delta_{l_1 l_2}\,\delta_{m_1 m_2},$$

and $Y_{lm}(\theta, \phi)$ has parity $(-1)^l$.

Section 1.4   The Hamiltonian operator $\widehat{H}_{\mathrm{so}}$ of a spin-$\frac{1}{2}$ particle contains a spin–orbit contribution $V_{\mathrm{so}}(r)\widehat{\mathbf{L}}\cdot\widehat{\mathbf{S}}$. If the particle is bound in a spherically-symmetric potential energy well, its Hamiltonian operator commutes with $\widehat{L}^2$ and $\widehat{S}^2$ but does not commute with $\widehat{L}_z$ or $\widehat{S}_z$; instead, it commutes with the total angular momentum operators $\widehat{J}^2$ and $\widehat{J}_z$, where $\widehat{\mathbf{J}} = \widehat{\mathbf{L}} + \widehat{\mathbf{S}}$. The eigenvalues of $\widehat{J}^2$ are $j(j+1)\hbar^2$ where, for a fixed l, we have $j = l + \frac{1}{2}$ or $j = l - \frac{1}{2}$. The corresponding eigenvalues of $\widehat{J}_z$ are $m_j\hbar$, where $m_j = -j, -j+1, \ldots, j-1, j$.

Eigenfunctions and eigenvalues of the Hamiltonian operator can be chosen to be simultaneously eigenfunctions of $\widehat{L}^2$, $\widehat{J}^2$ and $\widehat{J}_z$, and so can be labelled by the quantum numbers l, j and m_j. As a result of the spin–orbit interaction, states with the same value of l and different values of j have different energies. The spin–orbit interaction is small for electrons in atoms, but can be large for neutrons and protons in nuclei; this has a decisive effect on their energy-level structure and hence on their relative abundances.

Book 3 Chapter 2

Section 2.1   The Bohr model predicts energy levels for hydrogen that are consistent with the measured emission spectra, but the model is not satisfactory.

Section 2.2   The time-independent Schrödinger equation can be solved exactly for the Coulomb model of the hydrogen atom in which the electron and proton are treated as point-like particles interacting only via a Coulomb potential energy. Solutions are obtained using the method of separation of variables in spherical coordinates. The terms that depend on θ and ϕ are spherical harmonics, $Y_{lm}(\theta, \phi)$, while the r-dependence is governed by the radial equation

$$\left(-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right) R(r) = E\,R(r).$$

Section 2.3 Acceptable solutions of the radial equation are of the form

$$R_{nl}(r) = \left(\frac{r}{a_0}\right)^l \times \left(\text{polynomial in } \frac{r}{a_0}\right) \times e^{-r/na_0},$$

where the principal quantum number $n = 1, 2, 3, \ldots$ and the allowed values of l are $0, 1, \ldots, n-1$. The polynomial is of order $n - l - 1$ and has $n - l - 1$ nodes. The corresponding energy eigenvalues are $E_n = -E_R/n^2$, where E_R is the Rydberg energy.

Section 2.4 The complete eigenfunction is the product of $R_{nl}(r)$ and a spherical harmonic, $Y_{lm}(\theta, \phi)$. Spectroscopic notation labels states with $l = 0, 1, 2, 3, 4, \ldots$ by s, p, d, f, g, $\ldots$. The principal quantum number n is attached as a prefix, and the magnetic quantum number m is sometimes added as a subscript.

The radial probability density $R_{nl}^2(r) r^2$ is the probability per unit radial distance of finding an electron at distance r from the proton. The highest maximum in the radial probability density corresponds to the most probable electron–proton separation.

In general, the eigenfunctions have nodal surfaces from both the radial function and the spherical harmonic. Those due to the radial function are spherical surfaces. Those due to the spherical harmonic are either planar or conical surfaces.

Section 2.5 The eigenfunctions $\psi_{nlm}(r, \theta, \phi)$ can be used to calculate expectation values of quantities for the hydrogen atom. For large n, the expectation value $\langle r \rangle$ and the uncertainty Δr are both large, but the fractional uncertainty $\Delta r / \langle r \rangle$ decreases as n increases. The momentum probability density calculated for the ground-state eigenfunction is in very good agreement with experimental data.

Book 3 Chapter 3

Section 3.1 The variational method is especially useful for finding an approximate value of the ground-state energy of a quantum system. When we do not know the energy eigenvalue or eigenfunction for the ground state, we use information that we have about the system to make an educated guess at the form of the eigenfunction. The guessed function — a trial function $\phi_{1,t}(\mathbf{r})$ — may depend on one or more adjustable parameters. For a system characterized by a Hamiltonian $\widehat{H}$, the exact ground-state energy E_1 satisfies the inequality

$$E_1 \leq E_{1,t} = \frac{\langle \phi_{1,t} | \widehat{H} | \phi_{1,t} \rangle}{\langle \phi_{1,t} | \phi_{1,t} \rangle}.$$

The expression for $E_{1,t}$ is minimized with respect to the adjustable parameter(s) in the trial function, and the minimum value gives the optimum estimate of the ground-state energy. Under favourable circumstances, variational methods can also be used to find approximate energy eigenfunctions and eigenvalues for excited states.

Section 3.2 The perturbation method is a technique for obtaining approximate values for the energy eigenvalues and eigenfunctions of a quantum system. When we cannot solve the time-independent Schrödinger equation for a system with a complicated Hamiltonian, we simplify the Hamiltonian into a form for which we can find exact solutions, and use these solutions for the energy eigenvalues and eigenfunctions as the basis for obtaining more accurate solutions for the real Hamiltonian.

For a system characterized by the Hamiltonian $\widehat{H} = \widehat{H}^{(0)} + \delta\widehat{H}$, where $\widehat{H}^{(0)}$ is the unperturbed Hamiltonian with eigenvalues $E_n^{(0)}$ and eigenfunctions $\psi_n^{(0)}$, and $\delta\widehat{H}$ is the perturbation, the first-order approximation for the energy eigenvalues E_n is

$$E_n \simeq E_n^{(0)} + \langle \psi_n^{(0)} | \delta\widehat{H} | \psi_n^{(0)} \rangle.$$

It is also possible to obtain higher-order approximations.

Book 3 Chapter 4

Section 4.1 Hydrogen-like atoms are systems in which a negatively-charged particle is bound to a positively-charged nucleus by Coulomb attraction. Their properties are similar to those of atomic hydrogen, but with the energy eigenvalues given by

$$E_n = -\frac{E_R^{\text{scaled}}}{n^2},$$

where

$$E_{\mathrm{R}}^{\mathrm{scaled}} = Z^2 \, \frac{\mu}{\mu_{\mathrm{H}}} E_{\mathrm{R}},$$

and where Z is the atomic number of the nucleus, μ is the reduced mass of the atom, μ_{H} is the reduced mass of a hydrogen atom, and E_{R} is the Rydberg energy. The spatial extent of the eigenfunctions is found by replacing a_0 in the hydrogen atom eigenfunctions by

$$a_0^{\mathrm{scaled}} = \frac{1}{Z} \frac{\mu_{\mathrm{H}}}{\mu} \, a_0.$$

This model is used to understand properties of ions such as He^+ and Li^{2+}, which have a single electron, and muonic atoms and antiprotonic atoms. Muonic atoms provide information concerning the charge distribution within atomic nuclei, and antiprotonic atoms provide information concerning the distribution of neutrons within nuclei. The same model is the basis for understanding features of X-ray spectra.

Section 4.2   Under closer examination, the states of hydrogen with a particular value of principal quantum number n are not degenerate; their energies are independent of l but depend on the total angular momentum quantum number j. States with lower j have lower energy. Three of the perturbations responsible for the fine structure are (i) a relativistic correction to the kinetic energy, (ii) the spin–orbit interaction, and (iii) the Darwin term. The second of these does not apply to states with $l = 0$, whilst the third applies only to such states. The effect of the three perturbations on the energy of the eigenstates of hydrogen can be calculated using first-order perturbation theory. Yet finer structure, hyperfine structure, of the hydrogen atom spectrum is caused by the interaction of the magnetic dipole moments of the electron and proton. The $n = 1$ state is split into two levels, and transitions between these levels lead to emission of 21 cm radiation, which is exploited by astronomers.

Section 4.3   Dirac's relativistic wave equation provides a deeper understanding of the hydrogen fine structure. Electron spin and the spin–orbit energy-splitting are correctly predicted, as is the magnetic dipole moment of the electron. Quantum theory and relativity together predict that all subatomic particles with mass have corresponding antiparticles with the same mass. The possibility of creation and annihilation of photons, electrons and all other particles led to the development of quantum field theory. Quantum electrodynamics allows the calculation of further, hyperfine structure, such as the Lamb shift, and corrections to the electron magnetic dipole moment. It is also the fundamental theory to which quantum mechanics is a very good approximation when particle creation and annihilation do not play a major role.

Book 3 Chapter 5

Section 5.1   Taking the mass of the nucleus to be infinite, the Hamiltonian operator of an Z-electron atom can be written as

$$\widehat{\mathrm{H}} = \sum_{i=1}^{Z} \left[-\frac{\hbar^2}{2m_{\mathrm{e}}} \nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right] + \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{Z} \sum_{j>i}^{Z} \frac{e^2}{r_{ij}},$$

where motion of the whole atom has been neglected. The corresponding time-independent Schrödinger equation is non-separable, and cannot be solved exactly. In the independent-particle approximation, we neglect electron–electron repulsions. Energy eigenfunctions can then be found that are products of single-particle orbitals, and the energy of the atom is the sum of the energy eigenvalues associated with individual electrons.

Section 5.2   Electrons are identical fermions, so the electrons in an atom must be described by an antisymmetric total wave function. In first-order perturbation theory, an excited state of helium, in which the electrons occupy different orbitals ϕ_r and ϕ_s with energies E_r and E_s, has total energy

$$E_{rs} \simeq E_r + E_s + \frac{e^2}{4\pi\varepsilon_0} \int \frac{|\phi_r(\mathbf{r}_1)|^2 \, |\phi_s(\mathbf{r}_2)|^2}{r_{12}} \, \mathrm{d}V_1 \, \mathrm{d}V_2$$
$$\pm \frac{e^2}{4\pi\varepsilon_0} \int \frac{\phi_r^*(\mathbf{r}_1) \, \phi_s^*(\mathbf{r}_2) \, \phi_r(\mathbf{r}_2) \, \phi_s(\mathbf{r}_1)}{r_{12}} \, \mathrm{d}V_1 \, \mathrm{d}V_2,$$

where the plus sign is for a singlet state and the minus sign is for a triplet state. The last integral on the right-hand side is the exchange integral; this makes triplet states lower in energy than singlet states.

Section 5.3   In the central-field approximation, electron–electron repulsion is modelled by a spherically-symmetric effective potential energy function. This gives a separable time-independent Schrödinger

equation, and solutions can be obtained as products of single-particle orbitals. Each orbital is the product of a radial function and a spherical harmonic. For a given n, orbitals with low l-values have lower energies than orbitals with high l-values. Self-consistency can be achieved by an iterative procedure which ensures that the potential energy function is consistent with the distribution of electrons.

A shell is a set of orbitals with a given pair of n and l values. The configuration of an atom specifies how electrons occupy shells. Ground-state configurations explain the gross structure of the Periodic Table, in which elements with similar properties are organized into columns.

Section 5.4   When electron–electron and spin–orbit interactions are taken into account, the quantum numbers associated with a single electron are not good quantum numbers for the whole atom.

When the spin–orbit interaction is neglected, L and S, the total orbital angular momentum and total spin quantum numbers of all the electrons in the atom, are good quantum numbers, along with the corresponding M and M_S. Because of the residual electron–electron interaction, a single configuration splits into a number of energy levels, called atomic terms, labelled by ^{2S+1}L. Closed shells do not contribute to L and S. Two non-equivalent valence electrons with quantum numbers (l_1, s_1) and (l_2, s_2) gives rise to terms labelled by

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \ldots, l_1 + l_2 - 1, l_1 + l_2,$$
$$S = |s_1 - s_2|, |s_1 - s_2| + 1, \ldots, s_1 + s_2 - 1, s_1 + s_2.$$

When the spin–orbit interaction is included, the good quantum numbers are L, S, J and M_J, where J and M_J, refer to the total angular momentum (orbital plus spin) of all the electrons in the atom. If the spin–orbit interaction is weak, the LS-coupling scheme can be used and the allowed values of J are

$$J = |L - S|, |L - S| + 1, \ldots, L + S - 1, L + S.$$

Because of the spin–orbit interaction, states of different J have different energies, but have a $(2J + 1)$-fold degeneracy because the energy does not depend on M_J. Thus each *term* is split into a number of *levels* defined by different values of J. Levels are labelled by $^{2S+1}L_J$.

Hund's rules often allow us to determine the energy ordering of the terms and levels arising from a given configuration.

Book 3 Chapter 6

Section 6.1   The Born–Oppenheimer approximation is based on the fact that nuclei are much heavier than electrons and therefore move much more slowly. It allows us to study the behaviour of the electrons in a molecule by treating the nuclei as being in fixed positions. The nuclear motions can then be predicted by assuming that the electrons adapt instantaneously to each new position of the nuclei. The time-independent Schrödinger equation effectively splits into two parts, one for the electrons and the other for the nuclei, but these equations are coupled by the fact that the energy eigenvalues of the electronic equation depend on the nuclear positions, and these eigenvalues contribute to the effective potential energy function in which the nuclei move.

Section 6.2   The hydrogen molecule ion H_2^+ has a single electron. With the molecular axis in the z-direction, $\widehat{L}_z$ commutes with the electronic Hamiltonian and m is a good quantum number. The energy eigenvalues depend on the magnitude of m, but not on its sign.

The LCAO approximation to the ground state of H_2^+ is obtained by a variational calculation that uses a linear combination of two hydrogen-atom 1s orbitals, centred on the two protons, as the trial function. The optimized minimum-energy solution is

$$\psi_{el}(\mathbf{r}) = \frac{1}{\sqrt{2(1 + S)}} \left(\phi_{1s}^A(\mathbf{r}) + \phi_{1s}^B(\mathbf{r}) \right),$$

where the interatomic overlap integral $S = \langle \phi_{1s}^A | \phi_{1s}^B \rangle$. This solution corresponds to constructive interference, resulting in a high electron probability density in the region between the protons, and this helps to stabilize the molecule.

The first excited state is orthogonal to the ground state and is proportional to $\phi_{1s}^A(\mathbf{r}) - \phi_{1s}^B(\mathbf{r})$. This solution corresponds to destructive interference, resulting in a low electron probability density in the region between the protons, so the molecule is unstable in this state.

A plot of the electronic energy E as a function of the internuclear separation R is called an energy curve. The energy curve for a bonding molecular orbital has a minimum at the equilibrium nuclear separation; the energy curve for an antibonding orbital has no minimum.

Section 6.3 The LCAO approximation can be applied to any diatomic molecule by taking linear combinations of atomic orbitals, centred on the two different nuclei, with the same value of $|m|$. This results in a series of molecular orbitals.

In spectroscopic notation, molecular orbitals are labelled according to the value of $|m|$. Orbitals with $|m| = 0$ are labelled σ; those with $|m| = 1$ are labelled π, etc. The σ orbitals are non-degenerate, but all other types are doubly-degenerate. Orbitals of homonuclear diatomic molecules have a subscript g (for even parity) or u (for odd parity). The Greek letter is prefaced by a number, which orders orbitals of the same type by increasing energy.

Section 6.4 The electronic configurations of diatomic molecules are obtained by allocating electrons to molecular orbitals in order of increasing energy until all the electrons in the molecule are accounted for. Two electrons with opposite spin can occupy each molecular orbital.

The formal bond order is defined as $(n_b - n_a)/2$, where n_b is the number of electrons in bonding orbitals and n_a is the number of electrons in antibonding orbitals. For elements in the same row of the Periodic Table, a higher formal bond order generally implies a greater dissociation energy and a shorter internuclear distance.

Section 6.5 LCAO solutions can be improved by taking the nuclear charge to be an adjustable parameter or by using more atomic orbitals in the trial function. Additional effects such as symmetrization, electron–electron repulsion and the spin–orbit interaction cause electron configurations to split into terms and levels, but this does not undermine the gross description provided by the electronic configuration.

Book 3 Chapter 7

Section 7.1 A crystal is a solid structure in which a particular arrangement of atoms is repeated over a regular lattice. In ionic bonding, one type of atom loses electrons and another type of atom gains them; the resulting positive and negative ions bind together through electrostatic forces. In covalent bonding, valence electrons occupy bonding orbitals between nearest neighbours, with a high electron probability density between atoms. In metallic bonding, atoms beyond nearest neighbours contribute to bonding and the valence electrons spread out over the whole crystal.

The LCAO method correctly predicts that electron states are organized in energy bands, but ignores the requirement that the properties of a crystal should remain unchanged by any translation through a lattice vector.

Section 7.2 Bloch's theorem states that the energy eigenfunctions of electrons in an infinite crystal take the Bloch wave form

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}),$$

where $\mathbf{k}$ is the wave vector of the Bloch wave, and $u_{\mathbf{k}}(\mathbf{r})$ is a function with the periodicity of the lattice (i.e. $u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$ for any lattice vector $\mathbf{R}$). The values of $\mathbf{k}$ are restricted to a discrete set by periodic boundary conditions, and are further restricted to ensure that each Bloch wave has a unique wave vector.

The tight-binding method takes the electron energy eigenfunctions to be

$$\psi_{\mathbf{k}}(\mathbf{r}) = A_{\mathbf{k}} \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} \phi(\mathbf{r} - \mathbf{R}_i),$$

where $\phi(\mathbf{r} - \mathbf{R}_i)$ is an atomic orbital of a given type, centred on lattice site $\mathbf{R}_i$, and the sum is over all the lattice sites in the crystal. These eigenfunctions are consistent with Bloch's theorem. Interactions between valence electrons are ignored, and terms like $\langle \phi_i | \widehat{H} | \phi_j \rangle$ are dropped, where i and j refer to different, non-adjacent sites. The method predicts that the energy levels are practically continuous within finite energy bands, and that these bands are separated by band gaps. The width of an energy band increases as atoms are brought closer together, so some energy bands may overlap. At absolute zero, all the energy levels up to the Fermi energy are occupied, while higher energy levels are empty. At room temperature, only a few states around the Fermi energy have their occupations modified from those at absolute zero.

Section 7.3 A completely full energy band cannot conduct electricity. At absolute zero, a material with a partly-full band is a conductor, while a material whose bands are all completely full or completely empty is an

insulator. The electrical conductivity of a metal is proportional to the number density of electrons in the partly-full band. It is reduced by imperfections in the crystal associated with vacant lattice sites, foreign atoms or boundaries between crystalline grains; it is also reduced by vibrations of the atomic cores about their equilibrium sites, and therefore decreases with increasing temperature.

At a non-zero temperature T, a pure material with a band gap that is less than $80kT$ is classified as a semiconductor; conduction occurs because electrons in the valence band are thermally excited into the conduction band. Each excited electron leaves behind a positive hole, and conduction takes place through flows of electrons in the conduction band and holes in the valence band. The electrical conductivity increases with temperature as the number of charge carriers increases.

Semiconductors are often doped with specific impurity atoms. Donor atoms such as arsenic have an extra valence electron which can be donated to the conduction band. Acceptor atoms such as boron lack a valence electron which can be drawn from the valence band, leaving a hole behind. With sufficient concentrations of donor or acceptor atoms, it is possible to produce an n-type semiconductor in which conduction is dominated by electrons, or a p-type semiconductor in which conduction is dominated by holes.

Book 3 Chapter 8

Section 8.1   There are three types of radiative process: absorption of light, stimulated emission of light, and spontaneous emission of light. The first two of these can be analyzed in terms of the interaction between an atom (treated quantum-mechanically) and external radiation (treated classically). This is done in the electric dipole approximation, which represents the atom–light interaction by a time-dependent potential energy term

$$V(t) = e \sum_i \mathcal{E}(t) \cdot \mathbf{r}_i,$$

where $\mathcal{E}(t)$ is the electric field at the position of the atom and $\mathbf{r}_i$ is the position of the ith electron.

Section 8.2   If the electric dipole interaction is small, its effect can be found using time-dependent perturbation theory. This allows us to obtain an approximation for the wave function in a system that has been exposed to a small time-dependent perturbation. The overlap rule allows us to calculate the transition probability from an initial state to a final state. For monochromatic light, polarized in the z-direction and switched on at time 0, and off at time t, the probability of a transition from state i of energy E_i to state f of energy E_f is

$$P_{i \to f}(t) = \frac{e^2 \mathcal{E}_0^2}{\hbar^2} |\langle \psi_f | \hat{z} | \psi_i \rangle|^2 \left| \int_0^t e^{i\omega_{fi}t'} \cos(\omega t') \, dt' \right|^2,$$

where $\mathcal{E}_0$ is the electric field amplitude and $\omega_{fi} = (E_f - E_i)/\hbar$.

Section 8.3   If $\langle \psi_f | \hat{z} | \psi_i \rangle = 0$, light polarized in the z-direction does not induce first-order radiative transitions between states i and f, and the transition is said to be forbidden. The general rules restricting transitions between quantum states are called selection rules. For a one-electron atom, the selection rules are: $l_f = l_i \pm 1$ and $m_f = m_i - 1$, m_i or $m_i + 1$. For some directions of polarization, the changes in m may be further restricted.

Section 8.4   The probability that monochromatic radiation induces a radiative transition (either absorption or stimulated emission) depends on the angular frequency of the radiation, and on time. For monochromatic radiation, first-order perturbation theory predicts a transition probability that oscillates in time, but ordinary (non-monochromatic) light produces a transition probability that is proportional to time.

Section 8.5   The rates of radiative processes can be expressed in terms of various coefficients: B-coefficients for absorption and stimulated emission, and A-coefficients for spontaneous emission. Assuming a state of equilibrium, and using the Boltzmann and Planck distribution laws, Einstein related these coefficients to each other. This provides a way of calculating the rate of spontaneous emission in terms of the rate of absorption (or of stimulated emission).